

New (η^3 -Allyl)palladium Complexes with Pyridylpyrazole Ligands: Synthesis, Characterization, and Study of the Influence of N1 Substituents on the Apparent Allyl Rotation

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The allylpalladium $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L})](\text{BF}_4)$ ($\text{L} = \text{L}^1$ (**1**), L^2 (**2**), L^3 (**3**), L^4 (**4**)) complexes with pyridylpyrazole ligands 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (L^1), 2-(1-ethyl-5-phenyl-1H-pyrazol-3-yl)pyridine (L^2), 2-(1-octyl-5-phenyl)-1H-pyrazol-3-ylpyridine (L^3), and 2-(5-phenyl-3-(pyridin-2-yl)-pyrazol-1-yl)ethanol (L^4) were synthesized from the appropriate pyridylpyrazole ligand and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ in the presence of AgBF_4 . The cationic complex **1** was converted into the neutral complex **5** under basic conditions. These complexes were characterized, and the crystal and molecular structure of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)](\text{BF}_4)$ (**2**) was resolved by X-ray diffraction. Also, we have studied the apparent allyl rotation, observed as $\text{H}_{\text{syn}}\text{--H}_{\text{syn}}$ and $\text{H}_{\text{anti}}\text{--H}_{\text{anti}}$ interconversions. The influences of the solvent, the traces of water, and the N1 substituent have also been studied.

Introduction

In recent years, nitrogen binding ligands have received a great deal of attention, due to their promising properties in applied sciences, mostly because of their high efficiency in homogeneous catalysis.^{1–3} To date, a number of N-ligand derivatives have found practical applications and the search for new, more effective and/or selective species is still in progress. Chelating bi- or tridentate N-coordinating ligands such as diazabutanes, bis(oxazolinyl)pyrroles, and dipyridylamides and their prospective applications have been recently reported.⁴ The relevance of N-donors in organometallic chemistry has been exhaustively discussed. In these complexes, ligands affect the metal center electronically and sterically.

Allylpalladium chemistry is one of the most successful and innovative areas of organometallic catalysis.^{5,6} The most general coordination for allyl ligands is the η^3 bonding mode. The fluxional behavior of these systems directly related to the allyl group or to the ancillary ligands has also attracted much attention.⁷ One process frequently encountered in allylpalladium complexes is the mutual exchange of syn and anti groups. This process is believed to occur through an $\eta^3\text{--}\eta^1\text{--}\eta^3$ isomerization in (η^3 -allyl)palladium complexes.⁸ A second dynamic process

that is frequently observed in complexes with N-donor ligands is the apparent rotation of the allyl group. The apparent rotation is observed as a syn-syn, anti-anti exchange and/or isomerization process, depending on the molecular symmetry. Two main mechanisms have been proposed for the apparent allyl rotation: (a) an associative mechanism that involves five-coordinated intermediates (coordination of the solvent, the anion, or other molecules) that can undergo allyl pseudorotation^{9–11} and (b) dissociative mechanisms with formation of T-shaped three-coordinated intermediates after dissociation of mono- or bidentate (partial dissociation) ligands.^{12,13} Consequently, one scope of this work is to determine whether the apparent allyl rotation in derivatives with N-donor ligands involves Pd–N bond breaking or not.

Pyrazoles are known as both monodentate and exo-bidentate ligands, and their nitrogen atoms can coordinate to metal centers as either anionic or neutral donor groups. Pyrazole ligands having a 2-pyridyl group¹⁴ could be good candidates for the production of both cationic and neutral (η^3 -allyl)palladium complexes. They could also be helpful to study the apparent allyl rotation in the complexes obtained.

Results and Discussion

Synthesis and Spectroscopic Properties. Allylpalladium complexes with four different pyridylpyrazole ligands have been

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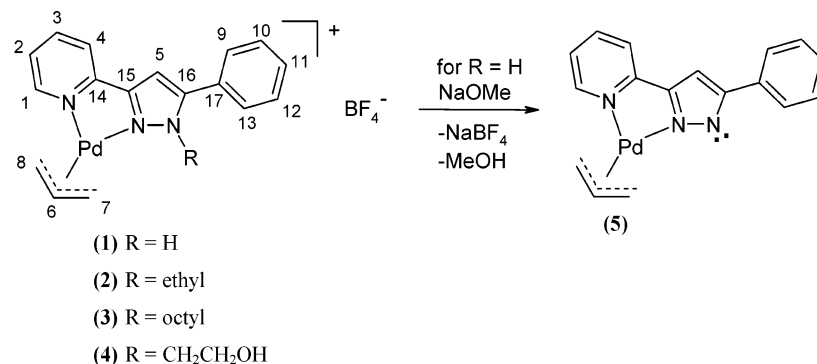
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**Figure 1.** Numbering scheme and reaction for the obtention of complex 5.**Table 1.** ¹H NMR (250 MHz, 298 K) Spectroscopic Data for Complexes 1–5 in Acetonitrile-*d*₃

	chemical shift (ppm) coupling constant (Hz)				
	1	2	3	4	5
N–H	13.21 (br)				
H ₁	8.75 (ddd, 5.4, 1.6, 0.9)	8.75 (d, 5.5)	8.74 (ddd, 5.7, 1.4, 0.6)	8.75 (dd, 5.4, 1.6)	8.59 (ddd, 5.4, 2.0, 0.9)
H ₃	8.21 (td, 8.1, 1.6)	8.20 (td, 7.7, 1.4)	8.19 (td, 8.5, 1.49)	8.20 (td, 7.7, 1.6)	7.96 (td, 7.5, 2.0)
H ₄	8.09 (ddd, 8.1, 1.4, 0.9)	8.06 (d, 7.7)	8.04 (d, 8.5)	8.08 (d, 7.7)	7.78 (ddd, 7.2, 1.3, 0.9)
H _{ph}	7.85–7.81 (m)	7.65–7.56 (m)	7.63–7.55 (m)	7.67–7.52 (m)	7.86 (d, 7.2), 7.40 (t, 7.2), 7.29–7.30 (m)
H _{ph} , H ₂	7.63–7.54 (m)				
H ₅	7.41 (s)	7.15 (s)	7.17 (s)	7.17 (s)	7.04 (s)
H ₆	5.92 (m)	5.98 (m)	5.95 (m)	5.96 (m)	5.77 (m)
H ₇ , H ₈ syn	4.56 (d, 7.0)	4.50 (d, 7.0)	4.46 (d, 7.2)	4.47 (d, 7.2)	4.17 (d, 7.0), 4.04 (d, 6.8)
H ₇ , H ₈ anti	3.51 (d, 12.4)	3.58 (d, 12.5)	3.54 (d, 12.2)	3.55 (d, 12.4)	3.31 (d, 12.2), 3.16 (d, 12.6)
N–CH ₂		4.33 (q, 7.2)	4.29 (t, 7.2)	4.39 (t, 5.4)	
N–(CH ₂) _x CH ₃		1.41 (t, 7.2)	0.84 (t, 6.6)		
N–CH ₂ CH ₂ –			1.78–1.74 (m)	3.87 (m)	
N–CH ₂ CH ₂ (CH ₂) ₅ CH ₃			1.32–1.02 (m)		

prepared: 2-(5-phenyl-1*H*-pyrazol-3-yl)pyridine (L¹),¹⁵ 2-(1-ethyl-5-phenyl-1*H*-pyrazol-3-yl)pyridine (L²),¹⁵ 2-(1-octyl-5-phenyl)-1*H*-pyrazol-3-yl)pyridine (L³),¹⁶ and 2-(5-phenyl-3-(pyridin-2-yl)pyrazol-1-yl)ethanol (L⁴). These ligands differ in the substituent in the N1 position and were prepared by following an efficient method published in the literature.^{15,16} The reaction of [Pd(η^3 -C₃H₅)Cl]₂ with these ligands in the presence of AgBF₄ in dichloromethane and at room temperature gave the new allylpalladium complexes [Pd(η^3 -C₃H₅)(L)](BF₄) (L = L¹ (1), L² (2), L³ (3), L⁴ (4)) as pale yellow powders in quantitative yield. Treatment of 1 in a mixture of CH₂Cl₂/CH₃OH (1:1) with sodium methoxide produced the neutral (η^3 -allyl)-palladium complex 5 (Figure 1).

The complexes have been fully characterized by elemental analysis, conductivity measurements, IR, ¹H NMR, and ¹³C-{¹H} NMR spectroscopy, and mass spectrometry. For the majority of these complexes, HMQC experiments were also performed, and in some cases NOESY experiments were carried out.

Elemental analysis and conductivity measurements confirm the stoichiometries proposed for the compounds. To confirm the existence of complexes 1–5, electrospray mass spectra were recorded. The positive ionization spectra of 1–4 gave peaks with *m/z* values of 368, 396, 480, and 412, respectively (molecular peak of the cation). For complex 5, the *m/z* value is 368 and corresponds to [Pd(η^3 -C₃H₅)(L¹) + H]⁺. Conductivity measurements of 10^{−3} M samples in acetone for complexes 1–4

(between 104 and 134 Ω^{-1} cm² mol^{−1}) are in agreement with 1:1 electrolytes, whereas for the complex 5 in acetonitrile the value is 29 Ω^{-1} cm² mol^{−1}, in agreement with the nonelectrolytic nature of the complex.^{17,18}

The ¹H NMR spectroscopic data for complexes 1–5 in acetonitrile-*d*₃ are collected in Table 1. The assignment of each proton was made on the basis of a previous publication of the free ligands.¹⁶ In these complexes, the H₁ chemical shift of the pyridyl group and the signal of the pyrazolyl proton are consistent with the coordination of both nitrogens to Pd(II). The chemical shifts are observed toward higher frequencies for all the complexes with respect to the free ligands.¹⁶ The same behavior is observed in other Pd(II) complexes with the same ligands ([PdCl₂(L)]; L = L¹–L⁴).^{15,19,20} Concerning the allyl group, a single doublet resonance is observed at room temperature for the H_{syn} protons and also for the H_{anti} protons for complexes 1–4. This observation is not in accordance with a static behavior of the complexes, where two nonequivalent H_{syn} protons and two nonequivalent H_{anti} protons would be expected, due to the asymmetry of the nitrogen ligands. This constitutes a clear indication of a dynamic situation that involves a syn-syn, anti-anti interconversion, such as an apparent allyl rotation process. This apparent allyl rotation is not observed in complex 5, which shows a doublet for each H_{syn} proton and also for each H_{anti} proton.

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Table 2. ¹H NMR (250 MHz, 298 K) Spectroscopic Data for Complexes 2–5 in Dichloromethane-*d*₂

	chemical shift (ppm) coupling constant (Hz)			
	2	3	4	5
H ₁	8.72 (ddd, 5.4, 1.4, 0.9)	8.73 (ddd, 5.4, 1.4, 0.7)	8.69 (dd, 5.4, 1.6)	8.53 (dt, 5.4, 1.1, 1.1)
H ₄	7.99 (ddd, 7.9, 1.2, 0.9)	8.00 (ddd, 7.8, 1.2, 0.7)	7.98 (d, 7.7)	7.70 (dt, 8.0, 0.9)
H ₃	8.18 (td, 7.9, 1.4)	8.18 (td, 7.9, 1.6)	8.15 (td, 7.7, 1.6)	7.92–7.85 (m), 7.40 (m), 7.25 (tt, 7.7, 1.1)
H _{ph}	7.65–7.60 (m), 7.57–7.52 (m)	7.63–7.60 (m), 7.55–7.51 (m)	7.65–7.52 (m)	
H ₂				7.16 (ddd, 7.4, 5.4, 1.4)
H ₅	7.00 (s)	7.00 (s)	7.00 (s)	6.96 (s)
H ₆	5.99 (m)	5.98 (m)	5.99 (m)	5.74 (m)
H ₇ , H ₈ syn	4.48 (d, 7.2)	4.50, 4.45 (d, 7.0)	4.57 (br)	4.32 (d, 7.0), 3.93 (d, 6.9)
H ₇ , H ₈ anti	3.81 (d, 11.7), 3.39 (d, 12.2)	3.76 (d, 12.5), 3.38 (d, 12.5)	4.10 (br)	3.27 (d, 12.5), 3.24 (d, 12.4)
N–CH ₂	4.34 (q, 7.3)	4.29 (t, 7.9)	4.44 (t, 5.4)	
N–(CH ₂) ₅ CH ₃	1.47 (t, 7.3)	0.89 (t, 6.4)		
N–CH ₂ CH ₂ –		1.81–1.71 (m)	3.98 (m)	
N–CH ₂ CH ₂ (CH ₂) ₅ CH ₃		1.32–1.16 (m)		

Table 3. ¹H NMR (250 MHz, 298 K) Spectroscopic Data for Complexes 1–4 in Acetone-*d*₆

	chemical shift (ppm) coupling constant (Hz)			
	1	2	3	4
N–H	13.30 (br)			
H ₁	8.83 (d, 5.5)	8.84 (d, 5.3)	8.85 (d, 5.6)	8.85 (d, 5.5)
H ₃	8.31 (td, 8.1, 1.6)	8.32 (td, 7.6, 1.5)	8.29 (td, 8.4, 1.4)	8.20 (td, 7.6, 1.5)
H ₄	8.09 (d, 8.1)	8.07 (d, 7.6)	8.03 (d, 8.5)	8.06 (d, 7.7)
H _{ph} , H ₂	7.85–7.5 (m)	7.73–7.62 (m)	7.73–7.65 (m)	7.77–7.62 (m)
H ₅	7.52 (s)	7.45 (s)	7.51 (s)	7.40 (s)
H ₆	6.05 (m)	6.04 (m)	6.19 (m)	5.96 (m)
H ₇ , H ₈ syn	4.65 (d, 6.8)	4.72 (d, 7.2)	4.69 (d, 7.2)	4.69 (d, 7.0)
H ₇ , H ₈ anti	3.62 (br)	3.76 (br)	3.76 (br)	3.72 (br)
N–CH ₂		4.48 (q, 7.1)	4.29 (t, 7.2)	4.35 (t, 5.4)
N–(CH ₂) ₅ CH ₃		1.43 (t, 7.3)	0.87 (t, 6.7)	
N–CH ₂ CH ₂ –			1.82–1.76 (m)	3.87 (m)
N–CH ₂ CH ₂ (CH ₂) ₅ CH ₃			1.45–1.00 (m)	

The ¹³C{¹H} NMR spectra were recorded in acetonitrile-*d*₃ for **1** and **4** and in dichloromethane-*d*₂ for **2**, **3**, and **5**, due to the low solubility of the complexes. Spectroscopic data are gathered in the Experimental Section. The assignment for each carbon was made on the basis of the literature data and HMQC experiments. Similar to the case for the ¹H NMR spectra, a single broad signal was observed for the terminal carbons of the allyl moieties in complexes **1** and **4**. This again reflects the apparent allyl rotation. However, two different signals (one for each terminal carbon) were observed for the spectra recorded in dichloromethane-*d*₂ (complexes **2**, **3**, and **5**). This observation indicates that the apparent allyl rotation is dependent on the solvent and was further studied by NMR, in a number of different solvents.

NMR Studies in Different Solvents. In order to analyze the dynamic behavior of the complexes, we performed ¹H NMR spectra of **1**–**5** in different solvents, acetonitrile-*d*₃ (Table 1), dichloromethane-*d*₂ (Table 2), and acetone-*d*₆ (Table 3), at room temperature. It was not possible to obtain ¹H NMR spectra of complexes **1** and **5** in dichloromethane-*d*₂ and acetone-*d*₆, respectively, due to their low solubility in these solvents.

As an example, Figure 2 shows the ¹H NMR spectra in different solvents for complex **2**. In this study, the most significant variations in the spectra are found for the allylic signals (see Table 4). For complexes **1**–**4**, in acetonitrile-*d*₃ (a coordinating solvent), only one signal for the anti hydrogens and only one signal for the syn hydrogens are observed. This does not occur for complex **5**, where two signals for each kind of proton are found. To confirm the data obtained for acetonitrile-*d*₃, an additional ¹H NMR experiment was performed for **4** in dimethyl-*d*₆ sulfoxide. This ¹H NMR spectrum is similar to that found in acetonitrile-*d*₃ (only one signal for H_{syn} and only one signal for H_{anti}).

However, when a noncoordinating solvent is used (dichloromethane-*d*₂), different spectra, depending on the complex, were obtained. For complexes **2**, **3**, and **5**, two H_{anti} signals are observed, whereas for H_{syn}, two signals are observed for **3** and **5** and only one signal is observed for **2**. On the other hand, complex **4** presents broad signals for both H_{syn} and H_{anti}.

When the ¹H NMR spectra were recorded in acetone-*d*₆ for **1**–**4**, only one doublet was observed for both H_{syn} protons and a broad band was observed for both H_{anti} protons.

These experiments indicate that the apparent allyl rotation is dependent on the solvent. Consequently, this process would involve an associative mechanism with the coordination of a molecule of solvent (coordination 4 → 5 → 4 on Pd(II)).

In order to see if there was any kind of interaction with a solvent such as acetone-*d*₆, NOESY experiments were performed, and they showed NOE interaction between the H_{syn} and H₂O molecules in the solvent (commercial grade deuterated solvents were used). This observation could indicate that, in this case, the apparent allyl rotation involves the coordination of a water molecule. Scheme 1 shows the proposed mechanism for this process: a five-coordinated Pd(II) intermediate is obtained by the coordination of X (X = water, coordinating solvent), followed by a pseudo-rotation of the allyl group which interchanges the two allyl terminal hydrogens. The decoordination of the X group leads to the final product, in which the observed H_{syn}–H_{syn} H_{anti}–H_{anti} interchange has taken place.

One special case is observed for complex **4** in dichloromethane-*d*₂. In this case, we observed the presence of broad bands for both H_{syn} and H_{anti}. Similar behavior is observed for complexes **1**–**4** in coordinating solvents or solvents containing H₂O molecules. This would indicate that the hydroxyethyl group of the pyridylpyrazole ligand interacts with the palladium atom,

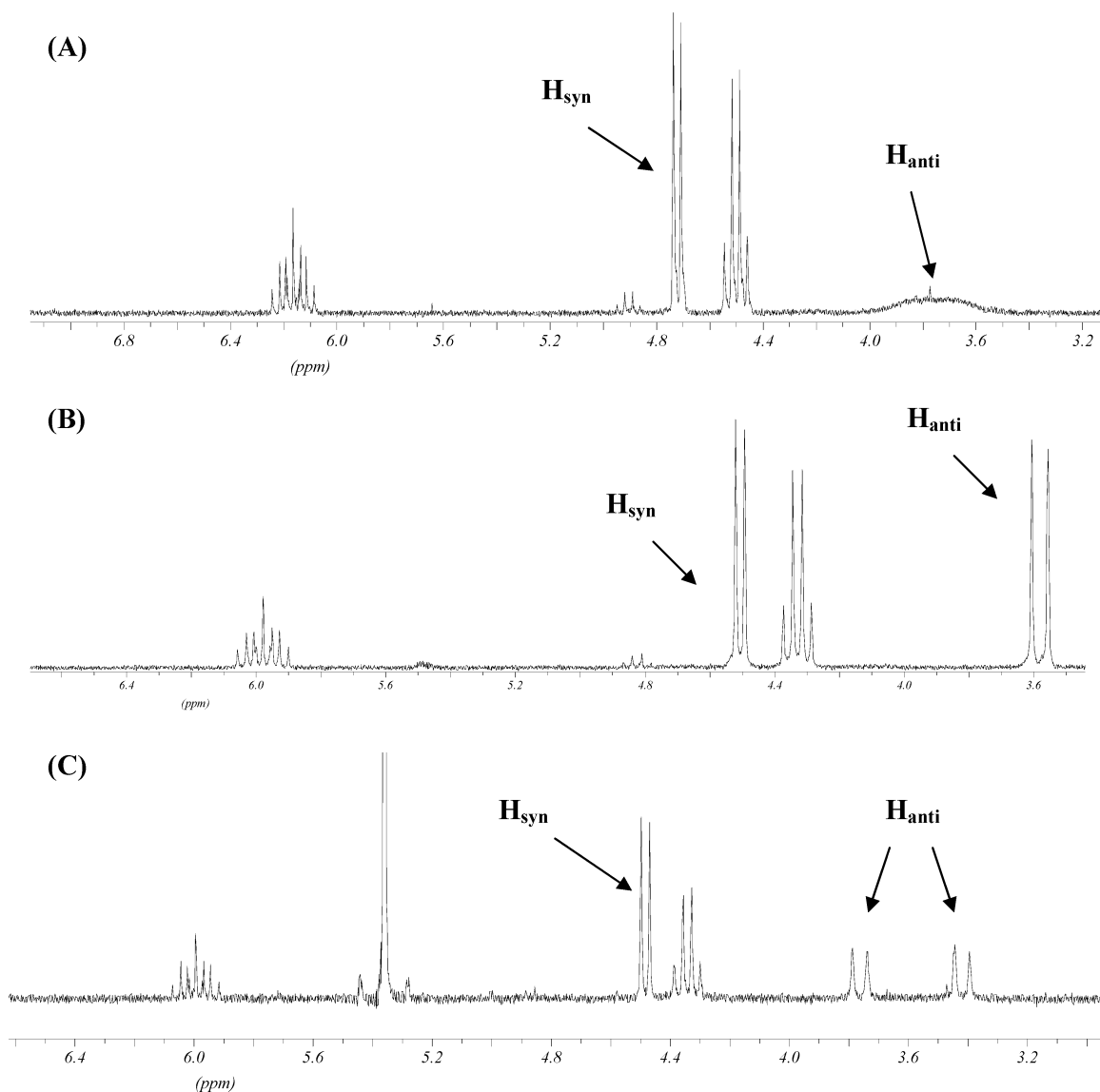


Figure 2. ^1H NMR spectra (250 MHz, 298 K) of complex **2** in (a) acetone- d_6 , (b) acetonitrile- d_3 , and (c) dichloromethane- d_2 .

forming an intermediate similar to that found with H_2O or a molecule of coordinating solvent. Therefore, for complex **4** in dichloromethane- d_2 , the process would take place through an intramolecular associative mechanism (Scheme 2).

Variable-Temperature NMR Studies. Variable-temperature ^1H NMR studies with different solvents (acetonitrile- d_3 , acetone- d_6 , and dichloromethane- d_2) were performed in order to obtain more information about the dynamic behavior of complexes **1–4** and the influence of the N1 substituent in the apparent allyl rotation. The study of the apparent allyl rotation was not performed at different temperatures with complex **5** because this complex presents a static situation in all of the solvents.

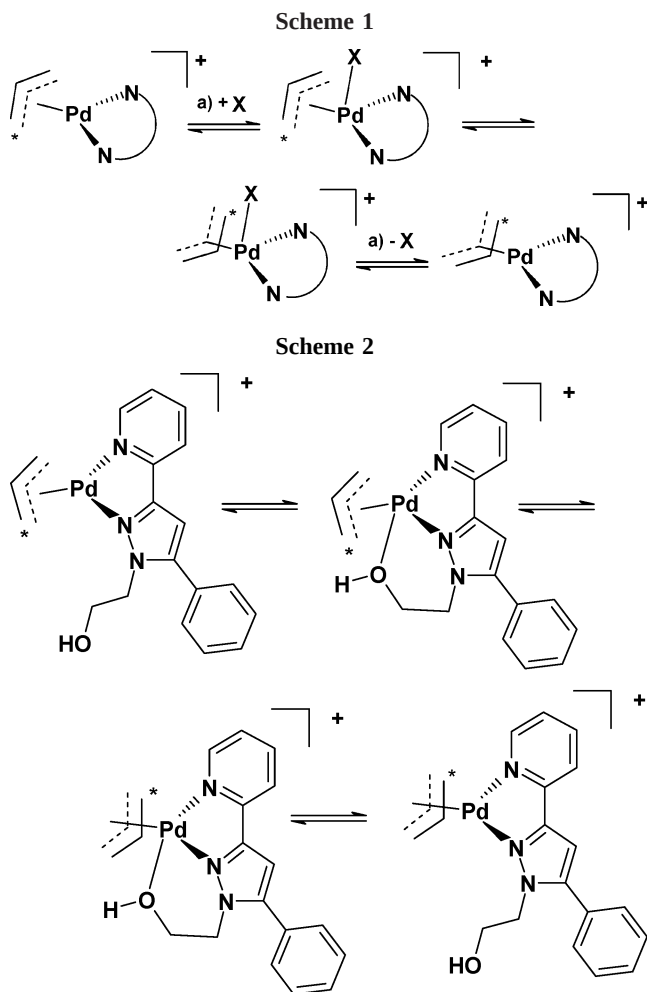
As an example, Figure 3 shows the variable-temperature ^1H NMR spectra of **2** in acetone- d_6 .

For complexes **1–4**, at low temperatures, two H_{anti} and two H_{syn} signals were observed, as is expected for a static situation. A subsequent increase of the temperature allowed the determination of the corresponding coalescence temperatures. These coalescence temperatures (T_c) and the separation of the two doublet signals allowed us to calculate the $\Delta G^\ddagger$ values of the processes²¹ (see Table 5). In some cases it was not possible to determine the $\Delta G^\ddagger$ values, because either the signals were not fully split at the minimum experimental temperature or the

Table 4. ^1H NMR (250 MHz, 298 K) Spectroscopic Data for Complexes **1–5**

complex	solvent	chemical shift (ppm) coupling constant (Hz)	
		H_7/H_8 syn	H_7/H_8 anti
1	CD_3CN	4.56 (d, 7.0)	3.51 (d, 12.4)
1	$(\text{CD}_3)_2\text{CO}$	4.65 (d, 6.8)	3.62 (br)
1	CD_2Cl_2	<i>a</i>	<i>a</i>
2	CD_3CN	4.50 (d, 7.0)	3.58 (d, 12.5)
2	$(\text{CD}_3)_2\text{CO}$	4.72 (d, 7.2)	3.76 (br)
2	CD_2Cl_2	4.48 (d, 7.2)	3.81 (d, 11.7), 3.39 (d, 12.2)
3	CD_3CN	4.46 (d, 7.2)	3.54 (d, 12.2)
3	$(\text{CD}_3)_2\text{CO}$	4.69 (d, 6.8)	3.76 (br)
3	CD_2Cl_2	4.50 (d, 7.0), 4.45 (d, 7.0)	3.76 (d, 12.5), 3.38 (d, 12.5)
4	CD_3CN	4.47 (d, 7.2)	3.55 (d, 12.4)
4	$(\text{CD}_3)_2\text{CO}$	4.69 (d, 7.0)	3.72 (br)
4	CD_2Cl_2	4.57 (br),	4.10 (br)
4	DMSO	4.57 (d, 7.0)	3.61 (d, 12.5)
5	CD_3CN	4.18 (d, 7.0), 4.04 (d, 6.8)	3.31 (d, 12.2), 3.16 (d, 12.5)
5	$(\text{CD}_3)_2\text{CO}$	<i>a</i>	<i>a</i>
5	CD_2Cl_2	4.32 (d, 7.0), 3.93 (d, 7.0)	3.27 (d, 12.5), 3.24 (d, 12.4)

^a ^1H NMR spectra of complex **1** in CD_2Cl_2 and complex **5** in $(\text{CD}_3)_2\text{CO}$ could not be recorded, due to the insolubility of these complexes in these solvents.



T_c value was not reached at the maximum temperature allowed by the solvent. For complexes 1–4, the values of $\Delta G^\ddagger$ in the solvents acetonitrile- d_3 and acetone- d_6 are similar and are independent of the N1 substituent. In contrast, in dichloromethane- d_2 , for complexes 2 and 3 the exact values could not be obtained, as T_c was not reached at 305 K (the maximum temperature allowed for this solvent). We have calculated the $\Delta G^\ddagger$ values for this temperature, and we can only suppose that the real values are higher than those obtained at 305 K and also higher than the values obtained for acetonitrile- d_3 and acetone- d_6 . For complex 4 in dichloromethane- d_2 , we could obtain exact $\Delta G^\ddagger$ values, because the T_c value is 298 K, due to the fact that the hydroxyethyl moiety favors an intramolecular associative mechanism of the apparent allyl rotation.

Crystal and Molecular Structures of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)]\text{-}(\text{BF}_4)$ (2). The crystal structure of complex 2 consists of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)]^+$ cations and BF_4^- anions held together by Coulombic forces. The cation $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)]^+$ is shown in Figure 4.

The metal atom is coordinated to a L^2 ligand via one pyrazole nitrogen, one pyridine nitrogen, and one allyl ligand in η^3 coordination. The two terminal allyl carbons are 0.282(3) and 0.169(3) Å from the plane defined by the atoms $\text{PdN}_{\text{py}}\text{N}_{\text{pz}}\text{C}(17)\text{C}(18)\text{C}(19)$. The central carbon (C(18)) is $-0.403(3)$ Å out of this plane. L^2 behaves as a bidentate ligand, forming a five-membered metallacycle.

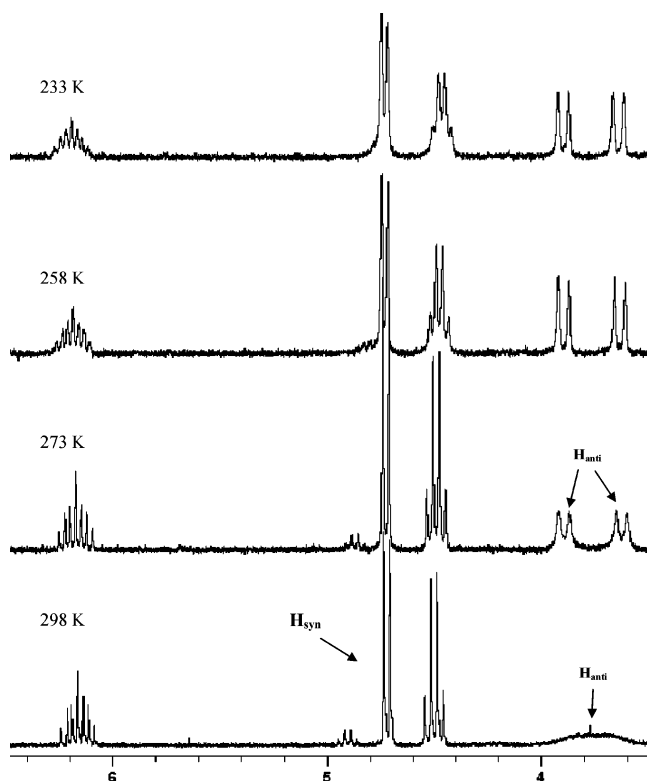


Figure 3. ^1H NMR spectra (250 MHz) of complex 2 in acetone- d_6 at various temperatures (233–298 K).

Table 5. ν , T_c , and $\Delta G^\ddagger$ Data for Complexes 1–4

complex	solvent	interchanging groups	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^\ddagger$ (kJ mol $^{-1}$)
1	acetonitrile- d_3	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	248		
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	298	18.2	63.8
	acetone- d_6	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	233	11.6	50.3
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	298	69.8	60.5
2	acetonitrile- d_3	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$			
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$			
	acetone- d_6	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$			
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	298	64.5	60.7
3	dichloromethane- d_2	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$			
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	> 305	100	> 61
	acetonitrile- d_3	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$			
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$			
4	acetone- d_6	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	213	10.6	46.0
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	298	61.0	60.8
	dichloromethane- d_2	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	> 305	12.5	> 66
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	> 305	95.0	> 61
4	acetonitrile- d_3	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$			
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$			
	acetone- d_6	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	233	15.6	49.7
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$			
4	dichloromethane- d_2	$\text{H}_{\text{syn}}\text{--}\text{H}_{\text{syn}}$	298	18.2	63.8
		$\text{H}_{\text{anti}}\text{--}\text{H}_{\text{anti}}$	298	70.5	60.5

The $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{N}_{\text{py}})(\text{N}_{\text{pz}})]$ core (containing pyrazole and pyridine nitrogen atoms and a η^3 -bonded allyl ligand) is found in one complex described in the literature.²²

The bond distance $\text{Pd}\text{--}\text{N}_{\text{py}}$ is almost identical with the $\text{Pd}\text{--}\text{N}_{\text{pz}}$ distance (2.115(3) and 2.117(3) Å, respectively). The $\text{Pd}\text{--}\text{C}$ bond lengths of the allyl group are in the range expected for these types of complexes.²³ The distance measured for $\text{Pd}\text{--}\text{C}(\text{terminal})$ in a disposition trans to N_{py} (2.114(3) Å) is of the same order as the distance found for the other $\text{Pd}\text{--}\text{C}(\text{terminal})$ and $\text{Pd}\text{--}\text{C}(\text{central})$ bonds (2.101(4) and 2.108(3) Å, respectively).

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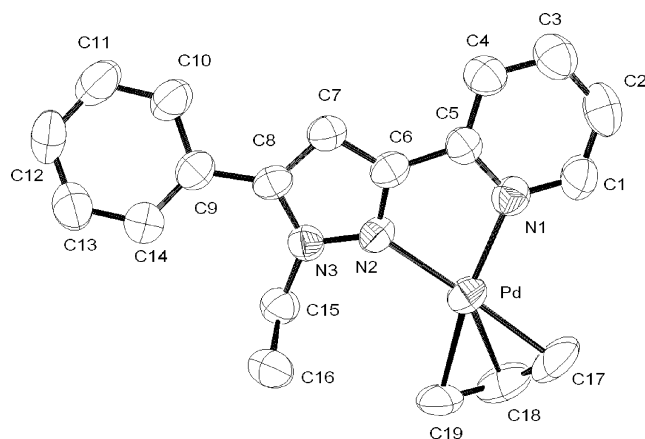


Figure 4. ORTEP drawing of the cation $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)]^+$ (ellipsoids are shown at the 50% probability level).

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)](\text{BF}_4)$ (2) with Estimated Standard Deviations (Esd's) in Parentheses

Pd–N(1)	2.115(3)	Pd–C(19)	2.144(3)
Pd–N(2)	2.117(3)	C(17)–C(18)	1.373(8)
Pd–C(17)	2.101(4)	C(18)–C(19)	1.402(6)
Pd–C(18)	2.108(3)		
N(1)–Pd–N(2)	77.68(10)	N(2)–Pd–C(19)	110.82(13)
N(1)–Pd–C(17)	102.78(18)	C(17)–Pd–C(19)	68.23(19)
N(1)–Pd–C(18)	134.61(18)	C(17)–Pd–C(18)	38.1(2)
N(1)–Pd–C(19)	170.71(14)	C(18)–Pd–C(19)	38.48(18)
N(2)–Pd–C(17)	171.11(17)	C(17)–C(18)–C(19)	118.3(4)
N(2)–Pd–C(18)	145.13(18)		

The Pd–N_{py}, Pd–N_{pz}, and Pd–C bond lengths in **2** are in the range of bond distances found in the literature for complexes containing N,N'-ligands trans to an allylpalladium fragment.^{24–26}

Selected bond distances and angles for this complex are gathered in Table 6. The allyl group has deviated from the ideal geometry (C–C distances of 1.36 Å and C–C–C angles of 120°): it presents two types of C–C distances at 1.373(8) and 1.402(6) Å and a C–C–C angle of 118.3(4)°. Similar distorted allyl groups have also been described in other complexes containing the $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$ fragment.^{27–29} The dihedral angle between the allylic plane and the palladium coordination plane is 66.90(9)°.

The N(1)–Pd–N(2) bite angle is 77.68(10)°. This angle is smaller than those found in the literature: with 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**¹), $[\text{PdCl}_2(\text{L}^1)]$,¹⁵ 79.16(14)°; 2-(1-ethyl-5-phenyl-1H-pyrazol-3-yl)pyridine (**L**²), $[\text{PdCl}_2(\text{L}^2)]$,²⁰ 78.83(9)°; 2-(1-octyl-5-phenyl-1H-pyrazol-3-yl)pyridine (**L**³), $[\text{PdCl}_2(\text{L}^3)]$,²⁰ 79.39(13)°.

The **L**² ligand is not planar. The pyridyl and phenyl groups are twisted with respect to the pyrazole ring. The py–pz dihedral angle is 7.05(17)°, and the ph–pz angle is 18.09(18)°. The py–pz dihedral angle is greater than those found in the complexes $[\text{PdCl}_2(\text{L}^1)]$ (py–pz 1.43(4)°),¹⁵ $[\text{PdCl}_2(\text{L}^3)]$ ¹⁹ (py–pz 1.5(2)°), and $[\text{PtCl}_2(\text{L}^2)]$ ²⁰ (py–pz 3.4(4)°), whereas the ph–pz angle is smaller than those found in the complexes $[\text{PdCl}_2(\text{L}^3)]$ (69.2(3)°) and $[\text{PtCl}_2(\text{L}^2)]$ ²⁰ (54.0(4)°) but greater than that found for $[\text{PdCl}_2(\text{L}^1)]$ ¹⁵ (0.48(3)°).

Table 7. Crystallographic Data for $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)](\text{BF}_4)$ (2)

formula	C ₁₉ H ₂₀ BF ₄ N ₃ Pd
<i>M</i> _r	483.59
temp (K)	293(2)
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
unit cell dimensions	
<i>a</i> (Å)	8.028(5)
<i>b</i> (Å)	10.519(4)
<i>c</i> (Å)	23.157(10)
α (deg)	90
β (deg)	95.14(2)
γ (deg)	90
<i>V</i> (Å ³)	1947.7(17)
<i>Z</i>	4
<i>D</i> _{calcd} (g·cm ^{−3})	1.649
μ (mm ^{−1})	0.999
<i>F</i> (000)	968
cryst size (mm)	0.2 × 0.1 × 0.1
θ range (deg)	2.55–29.99
index ranges	−9 < <i>h</i> < 10, 0 < <i>k</i> < 14, 0 < <i>l</i> < 32
no. of collected/unique rflns	14 739/4418 (<i>R</i> (int) = 0.0351)
no. of data/restraints/params	4418/20/295
goodness of fit	1.134
final <i>R</i> 1, <i>wR</i> 2	0.0384, 0.1104
<i>R</i> 1 (all data), <i>wR</i> 2	0.0449, 0.1171
resid electron density (e Å ^{−3})	0.468 and −0.647

The *n*-alkyl group, which is bonded to the N(3) atom, moves away from the chelating plane, giving a torsion angle N(2)–N(3)–C(15)–C(16) of 89.5(3)°.

Conclusions

Five new allylpalladium derivatives containing N-donor ligands have been prepared and their fluxional behavior studied. The apparent allyl rotation has been studied in detail. This process presents low $\Delta G^\ddagger$ values and is favored by coordinating solvents (or eventually traces of water present in the solvent), meaning that the apparent allyl rotation takes place through an isomerization of the square-planar geometry by an associative mechanism. The process is also favored for complex **4**, which contains a hydroxyethyl moiety. This group takes the role of the coordinating solvent when dichloromethane-*d*₂ is used. Therefore, in this case the process would take place through an intramolecular associative mechanism. The low $\Delta G^\ddagger$ values indicate that the process takes place without Pd–N bond rupture. On the other hand, the process does not occur in the neutral complex, probably due to the steric hindrance provoked in the rotation by the free pair of electrons of the pyrazolyl group.

Experimental Section

General Methods. Standard Schlenk techniques were employed throughout the synthesis using a double-manifold vacuum line with high-purity dry nitrogen. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{−3} M acetone and acetonitrile samples employing a Crison Micro CM 2200 conductimeter. Infrared spectra were performed on a Perkin-Elmer FT

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Series 2000 spectrophotometer as KBr pellets in the range 4000–400 cm^{-1} under a nitrogen atmosphere. The ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, HMQC, and NOESY spectra were run on a Bruker NMR-FT 250 MHz instrument. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Liquid chromatography/electrospray mass spectrometry experiments were performed by the Scientific Services of the Universitat de Barcelona on a Shimadzu AD VP chromatography instrument and API 150 (Applied Biosystems) mass spectrometer. The carrier was CH_3CN at a 0.2 mL min^{-1} flow rate. The samples were dissolved in CH_3CN at a concentration of 0.4 mg mL^{-1} , and $5\text{ }\mu\text{L}$ of each solution was injected on line. In the case of the electrospray interface, whole flow was introduced in the capillary source and nebulized at a 12 (arbitrary units) nitrogen flow. The auxiliary gas was nitrogen at a $7000\text{ cm}^3\text{ min}^{-1}$ flow rate. The main electrical conditions were as follows: positive electrospray capillary at 4200 V; potentials DP = 20 V, FP = 200 V, EP = –10 V; mass range measured between 100 and 950 amu; full scan mode; cycle time 2 s; source temperature $200\text{ }^\circ\text{C}$.

The compounds 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (L^1),¹⁵ 2-(1-ethyl-5-phenyl-1H-pyrazol-3-yl)pyridine (L^2),¹⁵ 2-(1-octyl-5-phenyl-1H-pyrazol-3-yl)pyridine (L^3),¹⁶ and 2-(5-phenyl-3-(pyridin-2-yl)pyrazol-1-yl)ethanol (L^4) were prepared according to the published methods (Figure 1). Samples of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ were prepared as described in the literature.³⁰

Synthesis of the Complexes. Complexes $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L})]\text{BF}_4$ ($\text{L} = \text{L}^1$ (1), L^2 (2), L^3 (3), L^4 (4)). A 0.37 mmol portion of the corresponding ligand (L^1 , 0.083 g; L^2 , 0.092 g; L^3 , 0.123 g; L^4 , 0.098 g) was added to a mixture of AgBF_4 (0.37 mmol, 0.070 g) and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ (0.18 mmol, 0.066 g) dissolved in dry dichloromethane (40 mL) at $0\text{ }^\circ\text{C}$. After the light-protected mixture was stirred at room temperature for 1.5 h, methanol (40 mL) was added. The yellow solution was then filtered through a pad of Celite. The solution was stirred for 1 h, most of the solvent was removed under vacuum, and diethyl ether (5 mL) was then added dropwise to induce precipitation. The yellow solid was filtered off, rinsed twice with 5 mL of diethyl ether, and dried under vacuum.

Data for **1** are as follows. Yield: 87% (0.147 g). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{BF}_4\text{N}_3\text{Pd}$ (455.6): C, 44.82; H, 3.54; N, 9.22. Found: C, 44.90; H, 3.62; N, 8.99%. Conductivity ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, $9.1 \times 10^{-4}\text{ M}$ in acetone): 132. IR (KBr, cm^{-1}): 3416 $\nu(\text{N-H})$, 3020 $\nu(\text{C-H})_{\text{ar}}$, 2960 $\nu(\text{C-H})_{\text{al}}$, 1616 $\nu(\text{C}=\text{C})_{\text{ar}}$, $\nu(\text{C}=\text{N})_{\text{ar}}$, 1454 $\delta(\text{C}=\text{C})_{\text{ar}}$, $\delta(\text{C}=\text{N})_{\text{ar}}$, 1084 $\nu(\text{B-F})$, 768 $\delta(\text{C-H})_{\text{oop}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (acetonitrile- d_3 solution, 63 MHz, 298 K): δ 154.4 (C_1), 153.8 (C_{15}), 150.6 (C_{14}), 147.8 (C_{16}), 141.4 (C_3), 130.7 (C_{11}), 130.0 (C_{10} , C_{12}), 127.4 (C_{17}), 126.6 (C_9 , C_{13}), 126.6 (C_2), 122.7 (C_4), 118.7 (C_6), 102.01 (C_5), 62.0 (C_7 , C_8) ppm. ES(+) MS (m/z (%)): 368 (100) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^1)]^+$, 222 (3) $[\text{L}^1 + \text{H}]^+$.

Data for **2** are as follows. Yield: 85% (0.152 g). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{BF}_4\text{N}_3\text{Pd}$ (483.6): C, 47.19; H, 4.17; N, 8.69. Found: C, 46.90; H, 4.05; N, 8.38. Conductivity ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, $9.2 \times 10^{-4}\text{ M}$ in acetone): 113. IR (KBr, cm^{-1}): 3066 $\nu(\text{C-H})_{\text{ar}}$, 2924 $\nu(\text{C-H})_{\text{al}}$, 1610 $\nu(\text{C}=\text{C})_{\text{ar}}$, $\nu(\text{C}=\text{N})_{\text{ar}}$, 1465 $\delta(\text{C}=\text{C})_{\text{ar}}$, $\delta(\text{C}=\text{N})_{\text{ar}}$, 1083 $\nu(\text{B-F})$, 768 $\delta(\text{C-H})_{\text{oop}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 solution, 63 MHz, 298 K): δ 154.0 (C_1), 151.8 (C_{15}), 150.9 (C_{14}), 148.2 (C_{16}), 141.3 (C_3), 130.8 (C_{11}), 129.7 (C_{10} , C_{12}), 129.3 (C_9 , C_{13}), 128.4 (C_{17}), 126.6 (C_2), 122.4 (C_4), 118.4 (C_6), 105.7 (C_5), 65.8 (C_7 or C_8), 59.4 (C_7 or C_8), 46.9 ($\text{N-CH}_2\text{CH}_3$), 16.4 ($\text{N-CH}_2\text{CH}_3$) ppm. ES(+) MS (m/z (%)): 396 (100) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)]^+$, 250 (13) $[\text{L}^2 + \text{H}]^+$.

Data for **3** are as follows. Yield: 80% (0.168 g). Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{BF}_4\text{N}_3\text{Pd}$ (567.8): C, 52.89; H, 5.68; N, 7.40. Found: C, 52.92; H, 5.59; N, 7.36. Conductivity ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, $1.0 \times 10^{-3}\text{ M}$ in acetone): 104. IR (KBr, cm^{-1}): 3099 $\nu(\text{C-H})_{\text{ar}}$, 2952

$\nu(\text{C-H})_{\text{al}}$, 1615 $\nu(\text{C}=\text{C})_{\text{ar}}$, $\nu(\text{C}=\text{N})_{\text{ar}}$, 1465 $\delta(\text{C}=\text{C})_{\text{ar}}$, $\delta(\text{C}=\text{N})_{\text{ar}}$, 1057 $\nu(\text{B-F})$, 765 $\delta(\text{C-H})_{\text{oop}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 solution, 63 MHz, 298 K): δ 154.0 (C_1), 151.8 (C_{15}), 150.9 (C_{14}), 148.7 (C_{16}), 141.3 (C_3), 130.8 (C_{11}), 129.7 (C_{10} , C_{12}), 129.4 (C_9 , C_{13}), 128.5 (C_{17}), 126.6 (C_2), 122.4 (C_4), 118.4 (C_6), 105.7 (C_5), 65.9 (C_7 or C_8), 59.2 (C_7 or C_8), 51.7 ($\text{N-CH}_2(\text{CH}_2)_6\text{CH}_3$), 32.0–22.9 ($\text{N-CH}_2(\text{CH}_2)_6\text{CH}_3$), 14.2 ($\text{N-CH}_2(\text{CH}_2)_6\text{CH}_3$) ppm. ES(+) MS (m/z (%)): 480 (100) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^3)]^+$.

Data for **4** are as follows. Yield: 78% (0.144 g). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{BF}_4\text{N}_3\text{OPd}$ (499.6): C, 45.68; H, 4.03; N, 8.41. Found: C, 45.90; H, 3.96; N, 8.23. Conductivity ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, $1.0 \times 10^{-3}\text{ M}$ in acetone): 134. IR (KBr, cm^{-1}): 3467 $\nu(\text{O-H})$, 3050 $\nu(\text{C-H})_{\text{ar}}$, 2924 $\nu(\text{C-H})_{\text{al}}$, 1616 $\nu(\text{C}=\text{C})_{\text{ar}}$, $\nu(\text{C}=\text{N})_{\text{ar}}$, 1464 $\delta(\text{C}=\text{C})_{\text{ar}}$, $\delta(\text{C}=\text{N})_{\text{ar}}$, 1060 $\nu(\text{B-F})$, 767 $\delta(\text{C-H})_{\text{oop}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (acetonitrile- d_3 solution, 63 MHz, 298 K): δ 153.8 (C_1), 151.7 (C_{15}), 151.1 (C_{14}), 149.5 (C_{16}), 141.1 (C_3), 130.7 (C_{11}), 129.7 (C_{10} , C_{12}), 129.6 (C_9 , C_{13}), 128.5 (C_{17}), 126.3 (C_2), 122.4 (C_4), 118.5 (C_6), 105.7 (C_5), 61.4 ($\text{N-CH}_2\text{CH}_2\text{OH}$), 59.2 (C_7 , C_8), 51.7 ($\text{N-CH}_2(\text{CH}_2)_6\text{CH}_3$), 32.0–22.9 ($\text{N-CH}_2(\text{CH}_2)_6\text{CH}_3$). ES(+) MS (m/z (%)): 412 (100%) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^4)]^+$.

The values of ^1H NMR spectra in acetonitrile- d_3 , dichloromethane- d_2 , and acetone- d_6 are presented in Tables 1–3, respectively, except for complex **1** in dichloromethane- d_2 , due to its low solubility in this solvent.

Complex $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^1)]$ (5). To a mixture of **1** (0.20 mmol, 0.091 g) and sodium methoxide (0.20 mmol, 0.011 g) were added dichloromethane (0.25 mL) and methanol (0.25 mL) at room temperature. The mixture was stirred with sonication for 5 min. The solvent was evaporated. The yellow solid was rinsed with 5 mL of diethyl ether and dried under vacuum.

Data for **5** are as follows. Yield: 60% (0.044 g). Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{Pd}$ (367.7): C, 55.52; H, 4.11; N, 11.43. Found: C, 55.49; H, 3.89; N, 11.55. Conductivity ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, $1.1 \times 10^{-3}\text{ M}$ in acetonitrile- d_3): 29. IR (KBr, cm^{-1}): 3025 $\nu(\text{C-H})_{\text{ar}}$, 2962 $\nu(\text{C-H})_{\text{al}}$, 1603 $\nu(\text{C}=\text{C})_{\text{ar}}$, $\nu(\text{C}=\text{N})_{\text{ar}}$, 1450 $\delta(\text{C}=\text{C})_{\text{ar}}$, $\delta(\text{C}=\text{N})_{\text{ar}}$, 761 $\delta(\text{C-H})_{\text{oop}}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 solution, 63 MHz, 298 K): δ 163.0 (C_{14}), 157.6 (C_{15}), 155.2 (C_{16}), 153.1 (C_1), 139.7 (C_3), 135.9 (C_{17}), 128.7 (C_{10} , C_{12}), 126.5 (C_{11}), 125.4 (C_9 , C_{13}), 121.9 (C_2), 119.2 (C_4), 116.4 (C_6), 99.3 (C_5), 60.2 (C_7 or C_8), 56.2 (C_7 or C_8) ppm. ES(+) MS (m/z (%)): 390 (7) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^1) + \text{Na}]^+$, 368 (100) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^1) + \text{H}]^+$.

The values of the ^1H NMR spectra in acetonitrile- d_3 , dichloromethane- d_2 , and acetone- d_6 are presented in Tables 1, 2, and 3, respectively.

X-ray Crystal Structure Analyses of the Complex $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)](\text{BF}_4)$. Suitable crystals for X-ray diffraction of the compound $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^2)](\text{BF}_4)$ were obtained through crystallization from dichloromethane. Data were collected on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite-monochromated Mo K α radiation. Unit-cell parameters were determined from 3888 reflections ($3 < \theta < 31^\circ$) and refined by least-squares methods. A total of 14 739 reflections were assumed in the range $2.55 \leq \theta \leq 29.99^\circ$, 4418 of which were nonequivalent by symmetry ($R_{\text{int}}(\text{on } I) = 0.035$). A total of 3902 reflections were assumed as observed, applying the condition $I > 2\sigma(I)$. Lorentz–polarization, but not absorption, corrections were made.

The structure was solved by direct methods, using the SHELXS97 computer program,³¹ and refined by full-matrix least-squares methods by the SHELXL97 computer program³² using 14 739 reflections (very negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0623P)^2 + 0.6986P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Eighteen H

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atoms were located from a difference synthesis and refined with overall isotropic temperature factors, and two H atoms were computed and refined, using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom, which are linked. The final $R(F)$ factor and $R(F^2)$ values as well as the number of parameters and other details concerning the refinement of the crystal structures are gathered in Table 7.

CCDC-628754 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Text and figures giving details of the synthesis and characterization of the ligand 2-(5-phenyl-3-(pyridin-2-yl)pyrazol-1-yl)ethanol (L^4) and a CIF file giving crystallographic data for $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(L^2)](\text{BF}_4)$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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